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(54) Title: METAL SPRAYING

(57) Abstract

A coating of zinc and an aluminium/magnesium alloy is arc sprayed by using a wire comprising a core of one material and a surface layer of the other.

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Title: METAL SPRAYING

Description of Invention

This invention relates generally to metal spraying, and more particularly to the application by arc spraying of a coating which comprises two metals or alloys. The metals in relation to which the invention has been developed are zinc and aluminium, or zinc and an aluminium/magnesium alloy.

Zinc and aluminium coatings have been widely used to protect steel structures from corrosion in aggressive and hostile conditions, e.g. on oil platforms at sea, in industrial plant, etc. Flame and arc spray processes have been widely used to produce coatings on original constructions as well as in repair and maintenance of existing structures. Zinc and aluminium have been separately sprayed to provide a layered coating, and more recently a zinc-15% aluminium alloy has been available in a wire form which can be arc sprayed. However, the surface of such zinc/aluminium alloy wire tends to oxidise, and difficulty is encountered in establishing electrical connection with such wire in an arc spraying pistol for carrying the electrical current necessary for arc spraying. This results in unsatisfactory coatings.

Difficulty is encountered in attempting to arc spray a composite or "pseudo-alloy" coating by feeding two wires, one of aluminium of one of zinc, to a conventional arc spraying device. Because the two wires are fed towards the arc from opposite sides of the head of the device, the resulting spray has a greater proportion of aluminium to one side and of zinc to the other side. When the spray head is traversed to apply the coating to a large area of substrate, this difference tends to become evened out but the non-uniformity of the spray pattern means that the technique can really only be used in automatic spraying equipment. When manually spraying, even the most skilled of operatives tends to produce a coating which lacks uniformity.

Nevertheless, it has been found that the arc spraying of a pseudo-alloy of aluminium and zinc or aluminium-magnesium and zinc produces a coating with a high degree of resistance to corrosion. What is important is to provide a fine dispersion of the two phases in the pseudo-alloy coating, and it is broadly the object of the present invention to achieve this whilst overcoming or reducing the above-described disadvantages associated with known methods and materials.

According to one aspect of the present invention, there is provided a method of arc spraying, wherein a wire comprising two metals or alloys as physically separate constituents is supplied to an arc spraying device.

Preferably the two metals or alloys comprise zinc and aluminium or zinc and an aluminium/magnesium alloy.

Preferably the wire comprises a core of one metal or alloy with an exterior layer of the other, and in particular the exterior layer should be a material with which electrical contact is readily established in order to facilitate the arc spraying process.

In the preferred material which is sprayed in accordance with the invention, the exterior layer of material preferably is zinc, since electrical contact is readily established therewith.

A further consideration which renders zinc the preferred material for the sheath or outer layer of the wire is that aluminium or aluminium/magnesium alloy work harden during processing and if such material were the outer layer it would make the wire less ductile and more prone to cracking of the outer layer.

As an alternative to a wire comprising a core of one material with an exterior layer of the other, the wire may comprise separate strands of the materials, twisted, braided, or otherwise intertwined together.

According to another aspect of the invention, we provide a wire suitable for use in an arc spraying operation, comprising aluminium or an alloy thereof

and zinc, as physically separate constituents. Preferably they are arranged as a core and an exterior layer.

Preferably the core is of an aluminium/magnesium alloy. The composition by weight of the wire may be Al 19%, Mg 1%, Zn balance.

The wire may be made by a process in which a core of aluminium or the alloy thereof is passed through a bath of molten zinc to provide a coating thereon, whereafter the wire may be coiled for storage and distribution for use in arc spraying operations.

Alternatively, a core of aluminium or the alloy thereof may be provided with its exterior layer or sheath of zinc by being wrapped in a strip thereof.

As yet a further alternative, the two materials may be co-extruded.

According to yet a further aspect of the invention, we provide a substrate having a coating thereon applied by an arc spraying method according to the first aspect of the invention.

The coating may contain 5-25% by weight of aluminium or an aluminium/magnesium alloy. Preferably it contains approximately 79% by weight zinc, 20% by weight aluminium, and 1% by weight magnesium.

The substrate is preferably steel.

By use of the invention, a substrate may be provided with a coating which comprises a fine and relatively uniform dispersion of zinc and aluminium or aluminium/magnesium. The inconvenience and disadvantages of being required to arc spray a zinc and aluminium alloy, or zinc and aluminium as separate arc spraying wires, are avoided.

The invention has been found to be particularly suitable for use in applying a coating to structures or parts of containers or vessels which in use are immersed in water, e.g. sea water. It has been found that not only does the invention facilitate the controlled spraying of a zinc/aluminium (alloy) coating, but in particular it has been found that an improved adhesive bond strength between the substrate and the sprayed material may be obtained.

By way of example, a substrate panel of cold rolled mild steel, one millimetre thick and finished to a surface roughness of 0.5 microns, was prepared by grit blasting with alumina particles. A Metallisation ArcSpray 528E pistol with a GC head was used to spray a coating using a wire as described hereafter. The conditions of spraying included a voltage of 21-28 volts, current 200A, pistol-substrate distance of 150 millimetres, and a pistol traverse rate of 50 millimetres per second. 2.3 millimetre wires were sprayed; one wire used comprised a zinc wire core wrapped with an Al-5wt%-Mg sheath, and another comprised an Al-5wt% Mg core wrapped with a zinc sheath.

Test substrates thus obtained were subjected to tests including corrosion tests in a salt spray cabinet. The salt spray test was carried out to BS 5466 (Part 6) and ISO 3768 using a 3.5% sodium chloride solution. The first sign of the appearance of red rust was watched for. The sample which used the zinc-cored wire wrapped with aluminium-magnesium alloy produced a time until the appearance of red rust of 7010 hours. The sample using the aluminium-magnesium cored wire with a zinc sheath resulted in a time until the appearance of red rust of 5950 hours. Such times until the appearance of red rust are at least comparable with and generally better than the results produced by the spraying of pseudo alloys using feed wires of different materials.

Similar advantageous results were obtained in respect of electro-chemical tests involving potential-time plotting and potentiodynamic measurements. Micro-structural analysis showed a high level of uniformity in the dispersion of the constituents of the coating.

The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or a method or process for attaining the disclosed result, as appropriate, may, separately, or in any

combination of such features, be utilised for realising the invention in diverse forms thereof.

CLAIMS

1. A method of arc spraying, wherein a wire comprising two metals or alloys as physically separate constituents is supplied to an arc spraying device.

2. A method according to Claim 1 wherein the two metals or alloys comprise zinc and aluminium, or zinc and an aluminium/magnesium alloy.

3. A method according to Claim 1 or Claim 2 wherein the wire comprises a core of one metal or alloy and an exterior layer of the other metal or alloy.

4. A method according to Claim 3 as appendant to Claim 2 wherein said exterior layer is zinc.

5. A method according to Claim 1 or Claim 2 wherein the wire comprises separate strands of the metals or alloys, intertwined together.

6. A wire suitable for use in an arc spraying apparatus, comprising aluminium or an alloy thereof and zinc as physically separate constituents.

7. A wire according to Claim 6 wherein said constituents are arranged as a core and an exterior layer.

8. A wire according to Claim 7 wherein the core is of an aluminium/magnesium alloy.

9. A wire according to Claim 7 or Claim 8 wherein the overall composition by weight of the wire is approximately Al 19%, Mg 1%, Zn balance.

10. A wire according to Claim 8 or Claim 9 which has been made by a process wherein a core is passed through a bath of molten zinc to provide a coating thereon.

11. A wire according to Claim 8 or Claim 9 wherein said core is provided with its exterior layer of zinc by being wrapped in a strip thereof.

12. A wire according to any one of Claims 7 to 9 wherein said core and exterior layer are co-extruded.

13. A substrate having a coating thereon applied by an arc spraying method according to any one of Claims 1 to 5.

14. A substrate according to Claim 13 wherein said coating contains 5-25% by weight of aluminium or of an aluminium/magnesium alloy.

15. A substrate according to Claim 14 wherein said coating contains approximately 79% by weight zinc, 20% by weight aluminium, 1% by weight magnesium.

16. A substrate according to any one of Claims 13 to 15 which is of steel.

17. A method of arc spraying, or a wire therefor, or a coated substrate, substantially as hereinbefore described.

18. Any novel feature or novel combination of features described herein and/or in the accompanying drawings.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/00536

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C4/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 91 00373 A (ALCAN INTERNATIONAL) 10 January 1991 see page 3, line 1 - line 15; claims 11-3,6-8	1,5,13, 16-18
X	EP 0 064 840 A (PPG INDUSTRIES) 17 November 1982 see claims 1-10,18-24	1,3-7, 13,16-18
X	FR 1 194 596 A (LA METALLISATION DE PRECISION) 10 November 1959 see page 1 - page 2	1,5,13
X	FR 1 068 960 A (MARTIN DE DESCHULTHESS) 2 July 1954 see claim RESUME	1,13

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 011, no. 185 (C-428), 13 June 1987 & JP 62 007843 A (YANMAR DIESEL ENGINE CO LTD), 14 January 1987, see abstract	1,13
X	GB 816 391 A (THE BRITISH OXYGEN COMPANY) 15 July 1959 see claims 1-5; figures 1-4	1,13
X	US 5 294 462 A (JOHN J. KAISER) 15 March 1994 see claims 1-15	1,15
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 241 (C-604), 6 June 1989 & JP 01 052051 A (DAINIPPON TORYO CO LTD), 28 February 1989, see abstract	1,2,13

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. ational Application No
PCT/GB 98/00536

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9100373 A	10-01-1991	AU 5843690 A	17-01-1991
EP 64840 A	17-11-1982	US 4396473 A	02-08-1983
		CA 1208600 A	29-07-1986
		JP 57181387 A	08-11-1982
FR 1194596 A	10-11-1959	NONE	
FR 1068960 A	02-07-1954	NONE	
GB 816391 A		NONE	
US 5294462 A	15-03-1994	NONE	